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NUCLEAR MAGNETIC RESONANCE

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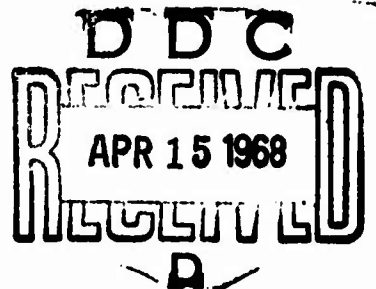
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NUCLEAR MAGNETIC RESONANCE<sup>1,2</sup>

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Due to the exponential growth of publications dealing with NMR, it has become a necessary, common practice to cover only selected topics in the annual review and to include only selected references. Such selection usually reflects the personal interests of the reviewer, and this chapter is no exception. NMR publications are now appearing at a rate of 550 per month, which is more than an order of magnitude larger than we can cover. Most of the work omitted consists of system-oriented studies in which NMR is applied to a particular chemical system or problem, i.e. NMR is used as a tool.

We have sought to include publications emphasizing phenomena, new experimental and theoretical methods, and new areas of application. About half of our review is devoted to two very active

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fields, exchange processes and nuclear relaxation. These are followed by shorter commentaries on chemical shifts, the indirect spin-spin coupling, solid-state studies, and biological applications. We conclude with brief mention of the promising new field of ion cyclotron resonance.

Our task is eased somewhat by the large number of useful books on NMR and reviews of particular areas which have appeared in 1967. The book by Corio (1) covers in detail both the mathematical and physical aspects of the quantum mechanical analysis of high resolution NMR spectra. An introduction to magnetic resonance by Carrington and McLachlan (2) is a successful attempt to discuss the fundamentals of both ESR and NMR and to emphasize the features common to the two fields. A basic introduction to NMR is given by Hecht (3), and the practical aspects of NMR at an introductory level are discussed by Chapman & Magnus (4). Organic applications with major emphasis on the structural implications of NMR spectra are given by Mathieson (5). Manenkevich & Orbach (6) have edited a collection of reprints of

major papers on spin-lattice relaxation in ionic solids. Many topics covered in the very detailed, comprehensive treatise on experimental techniques in ESR by Poole (7) will definitely be of interest to those engaged in NMR research.

The series of review articles edited by Waugh (8) continues with the second volume. It contains a very thorough treatment of the problem of sensitivity enhancement in NMR by Ernst (9), two reviews on the theory of chemical shifts by Lipscomb (10) and Musher (11), and a discussion of the theory of nuclear relaxation in hydrogen by Deutch & Oppenheim (12) with an interpretation of the experimental data. The second volume of the series edited by Emsley, Feeney & Sutcliffe (13) has also been published. O'Reilly (14) deals with the quantum mechanical calculations of chemical shifts whereas Zürcher (15) discusses the different contributions to proton shifts and their calculation in unconjugated organic compounds. High-resolution NMR spectra of partially oriented molecules are treated by Buckingham & McLachlan (16); the NMR spectra of paramagnetic systems are discussed by

de Boer & van Willigen (17). The review by Lynden-Bell (18) of line-shape calculations using density matrix methods is a very timely topic in view of the current interest in chemical exchange processes.

Mention must also be made of the excellent coverages of the NMR field for 1965 (19) and 1966 (20). Other reviews are devoted to NMR studies of particular types of system. Stengle & Langford (21) discuss NMR studies of ligand substitution processes, Brown (22) treats NMR studies of organometallic exchange processes, and Hinton & Amis (23) cover NMR studies of ions in pure and mixed solvents. Applications to polymers are given by Allen (24) and by McCall (25); Luckhurst (26) reviews the use of liquid crystals as a solvent in NMR. The theory of nuclear relaxation in simple gases has been reviewed by Bloom & Oppenheim (27) who emphasize the information on intermolecular forces obtainable from relaxation time measurements.

## EXCHANGE PROCESSES

By and large most of the current NMR studies of chemical exchange rates are directed at particular systems or have as their objective the extension of known methods to more complex rate processes. Only a few new papers deal with the theory of exchange effects on NMR phenomena. Hoffman (28) has given an alternative derivation of Allerhand & Thiele's (29) expression for the high-resolution line-width in the limit of fast exchange. And, as mentioned in the Introduction, Lynden-Bell (18) has reviewed the use of density matrix methods to calculate line shapes. However, substantial progress has been made on the basic, general problem of assessing the overall accuracy of NMR rate determinations by comparing them with rates measured independently by some different method. The main reason why such comparisons were not made earlier lies in the fact that NMR covers a range of rates and a variety of exchange processes not accessible to other more established methods.

The first comparison of this nature is apparently that of Ollis & Sutherland (30) who compared the thermodynamic parameters for the ring inversion of tri-*o*-thymotide from NMR studies with the polarimetry results for its racemization. The agreement is acceptable; however, it isn't clear that the same exchange process is involved in the two measurements. Curtin et al. (31) have determined the syn-anti isomerization rates for several substituted imines from the NMR coalescence temperatures and the slower rates for another imine by means of equilibration studies employing ultraviolet spectra. The two sets of rates were reduced to a common temperature, the substituent effects were calculated by a Hammett  $\sigma_p$  treatment, and the results were found to agree within the accuracy of the over-all method. This approach has the disadvantage of introducing the approximations associated with the Hammett  $\sigma_p$  method.

A more direct test of the NMR line-shape method has been made in studies of amides with two distinguishable isomers. The temperature dependence of internal rotation about the C-N



amide bond is great enough in some amides that one can measure the fast exchange rates at high temperatures by NMR and the slow rates at low temperatures by a more conventional equilibration technique. Mannschreck, Matthews & Rissmann (32) have found that the activation parameters obtained from an equilibration study of N-benzyl-N-2,4,6-tetramethylbenzamide compare favorably with those for the similar compound N,N-2,4,6-pentamethylbenzamide from an NMR line-broadening technique. This approach has been carried out on a single compound by Gutowsky, Jonas & Siddall (33), who investigated the rate of internal rotation about the C-N amide bond in N-methyl-N-benzylformamide between 170° and 90° by an NMR complete line-shape analysis method and between 20° and -2.5° by an equilibration technique. The equilibration studies were performed on samples in which the isomer with the methyl cis to the formyl proton was concentrated by complexing the equilibrium mixture with uranyl ion and stripping it off at low temperatures. It is indeed gratifying that the exchange rates and activation parameters obtained from the NMR study agree well with

those obtained by the classical equilibration method even though the fast rates measured by NMR differ by six orders of magnitude from the slow rates measured conventionally.

Other studies of general interest reflect growing appreciation of the fact that care must be taken to avoid systematic errors in the NMR data analysis (34, 35). For this reason, some of the earlier work has been repeated. One such case is the redetermination of the barrier to internal rotation in N,N-dimethyl formamide by Conti & von Philipsborn (36). The authors used complete line-shape analysis with decoupling of the formyl proton and compare the results with those they obtain for monodeutero N,N-dimethyl formamide. They find a barrier to internal rotation of  $E_a = 24 \pm 2$  kcal/mole, with a frequency factor of  $\log A = 14.5$ . The corresponding  $\Delta G^\ddagger$  is 21.8 kcal/mole. They conclude that values for  $E_a$  of less than 20 kcal/mole previously reported for the compound are a result of systematic errors.

In another such case, Anet & Bourn (37) performed very thorough NMR line-shape and double-resonance studies of the ring inversion in cyclohexane- $d_{11}$ , attempting to resolve discrepancies in the reported thermodynamic parameters. Complete line-shape analysis was used in conjunction with deuterium decoupling and a critical discussion of the calculation of line shapes is presented. Moreover, the use of a double resonance technique introduced by Forsen & Hoffman (38) enabled them to measure much smaller rate constants, greatly extending the temperature range investigated. Their values of  $\Delta G^\ddagger$ ,  $\Delta H^\ddagger$ , and  $\Delta S^\ddagger$  for the chair-to-boat conversion are 10.3 and 10.8 kcal/mole and 2.8 e.u., respectively. The NMR studies of the inversion of cyclohexane have been critically reviewed by Harris and Sheppard (39) who conclude that uncertainties in the experimental determination of  $\Delta S^\ddagger$  and the conceptual uncertainties inherent in the absolute rate theory make the entropy of activation unreliable for the determination of the conformation of the activated complex.

In our opinion the  $\Delta G^\ddagger$  value obtained from NMR line-shape studies is a reliable parameter not too sensitive to various systematic errors or to the limited temperature range often used in NMR measurements. But  $\Delta H^\ddagger$  and  $\Delta S^\ddagger$ , in particular, should be used with caution and full understanding of their limited accuracy. Furthermore, understanding of the factors leading to systematic errors in rate determinations (34, 35) is reaching the point where reliance can be placed upon the quantitative accuracy of results obtained from careful measurements and adequate data analyses.

We consider next the work done on each of several types of exchange process amenable to NMR methods. A perennial favorite is hindered rotation about different single or partially-double bonds, for which we cite several examples. Restricted rotation about the aryl-nitrogen bond has been studied in N-benzyl-N-(o-tolyl) acetamide (40), different types of amides (41, 42), in N-aryl-N,N-dimethylformamidines (43), and in polynitro acetanilides (44). Hindered rotation has been reported about the benzene-to-carbonyl bond (45) in m-substituted benzamide, about

the carbon-carbon double bonds in ketene mercaptals and amins (46), and about the carbon-carbon bonds in pentadienyllithium (47). A complete line-shape analysis has been made of the hindered rotation in N,N-dimethylcarbamoyl chloride and N,N-dimethylthiocarbamoyl chloride (48). The coalescence temperatures in N,N-dimethylcarbamates have been determined (49), and complete line-shape analysis has been applied to various N-substituted carbamates (50). A spin-echo study of internal rotation in 1,1-difluoro-1,2-dibromodichloroethane was made by Vold & Gutowsky (51) who determined activation parameters which are in good agreement with the values obtained from earlier steady-state NMR measurements (52). From the number and diversity of these studies it is evident that hindered rotation is a much more common phenomenon than was appreciated only a few years ago.

In the past, sensitivity considerations have discouraged gas phase measurements of exchange rates by NMR. However, instrumental evolution has now made such studies possible as shown by Harris & Spragg (53) who determined the barrier to hindered rotation

about the N-N bond in dimethylnitrosamine in the vapor. The free energy of activation  $\Delta G^\ddagger$  is 23.3 kcal/mole for the liquid and 21.1 kcal/mole for the vapor phase. The intermolecular contribution to the barrier to internal rotation is therefore about 2 kcal/mole, the barrier being higher in the liquid than in the vapor.

A very active area is that dealing with ring inversion and conformational equilibria of cyclic compounds. Such studies have been made for a number of substituted 1,1-difluorocyclobexanes, using complete line-shape analysis (54); Roberts (55) reviews much of this work, particularly the use of  $^{19}\text{F}$  spectra of gem-substituted difluorocycloalkanes. Activation parameters for ring inversion have been determined in the following cyclic systems: 2-substituted [3.2] metacyclophanes (56); 1,1,4,4-tetramethylcyclohexane (57); hexahydro-1,3,5-triazines (58); 9-10-disubstituted cis-decalins (59); in 1,3-dioxane (60); in 7,12-dihydropheiadene and its 1-methoxy derivative (61); in annulenes and dehydro-annulenes (62); in hexahydro-1,3,5-trimethyl-

1,3,5-triazine (63); and in azepines and diazepines (64). The nitrogen inversion has been investigated in 1-acylaziridines (65). A similar study of 2,3-diazabicyclo [2.2.1] heptane and bicyclo [2.2.2] octane has led to the suggestion that in these compounds inversion occurs consecutively at two nitrogens (66). The fast, reversible equilibrium between  $\alpha$ -methyl oxepin and its valence-tautomer toluene-1-oxide has been investigated at different temperatures (67). Pasto et al. (68) have reported on the conformation of the 1,3-oxathiolane ring system and on the free energy changes produced by substituents in the 2 position.

In some of these cyclic systems, complex or sequential conformational changes evidently occur. At the present time it is unclear just how significant the NMR work will be in improving our understanding of such conformational behaviour in complex molecules. It would appear that these applications have opened a fruitful field in conformational analysis. However, there is a definite need in many of the studies to use better experimental techniques and more sophisticated data analysis in order to

obtain quantitative results.

In a somewhat different vein, we note that in conformational studies of 7,12-dihydropleiadenes (69) the nuclear Overhauser effect (70) was used to carry out unambiguous structural assignments. This application and the earlier publications by Anet (71) and Nakanishi et al. (72) have shown that the generalized nuclear Overhauser effect has great promise for solving stereochemical problems. It can identify adjacent protons which show no scalar coupling but which have a large direct dipole-dipole interaction.

Another active area is that dealing with proton exchange. Grunwald et al. (73) have followed the kinetics of proton exchange between methanol and p-nitrophenol or p-bromophenol in buffered solutions containing phenol and phenoxide and in acid solutions containing phenol and HCl at  $-80^{\circ}$ . In order to obtain plausible rate laws they introduced an empirical correction to the rates determined via the Bloch equation. The physical significance of this correction is not clear. Another study, by



Puar & Grunwald (74), deals with the exchange of carboxyl and hydroxyl protons of salicylic acid with the hydroxyl proton of methanol. A related study by Grunwald (75) deals with acid dissociation and proton exchange of trimethylammonium ion in methanol, while for the trimethylammonium ion the kinetics of deuterium exchange has been investigated in heavy water (76) and in  $D_2SO_4$  (77). Massicot & Zonsajn (78, 79) have measured the proton exchange of aromatic protons of pyrogallol and 2-naphtol in alkaline medium (NaOD). The deuterium exchange of methoxyacetone (80) has been studied in aqueous solution.

Substantial progress has been made in the areas of hydration and solvation processes, often by means of  $^{17}O$ . A typical use of enriched  $^{17}O$  spectra is that of Greenzaid et al. (81) who investigated the reversible hydration of aliphatic aldehydes and ketones. Proton spectra have also proved useful in measuring equilibrium constants for the hydration-dehydration reaction of the carbonyl group. The reversible hydration of acetaldehyde has been investigated in more detail by measuring the acid

catalyzed oxygen exchange between acetaldehyde and solvent water (82). In a similar fashion, the relative concentrations of the two different enol tautomers of asymmetric  $\beta$ -diketones (83) were determined from  $^{17}\text{O}$  spectra. Nakamura & Meiboom (84) have found that the solvation number of the magnesium ion is 6 in anhydrous methanol. Using  $^{17}\text{O}$  NMR, Glass & Tobias (85) have determined the hydration number and rate of water exchange of the trimethylplatinum (IV) ion in aqueous solution.

Other studies have dealt with exchange of solvent between coordination spheres of metal ions and the bulk of solution. Wüttrich & Connick (86) have measured the  $T_2$  relaxation time for  $^{17}\text{O}$  in aqueous vanadyl perchlorate solutions in the temperature range 5-170°. They found that in the major part of this temperature region the relaxation due to the influence of vanadyl ions is controlled by the rate of exchange of water molecules between the first coordination sphere of the metal ions and the bulk of solution. The exchange rates of water and thiocyanate ion with nickel (II)-thiocyanate complexes have been studied

by Jordan, Dodgen & Hunt (87) using  $^{17}\text{O}$  and  $^{14}\text{N}$  NMR spectra.

Interesting results demonstrating the capabilities of NMR for hydration studies have been obtained by Reuben & Fiat (88).

They investigated hydration of the vanadyl (IV) ion in aqueous solution using  $^{17}\text{O}$  NMR spectroscopy. Two kinds of water molecules were distinguished, namely the four equatorially coordinated water molecules ( $\tau \approx 10^{-3}$  sec) and the rapidly exchanging axial water molecules ( $\tau \approx 10^{-11}$  sec). The vanadyl ion has been the subject of study by Swift, Stephenson &

Stein (89) in which the protonation rate of aquated vanadyl ions in aqueous solution was measured by means of the proton line widths. Finally, Rabideau & Hecht (90) have investigated the effect of proton exchange in water on  $^{17}\text{O}$  NMR linewidths and found the proton  $^{17}\text{O}$  coupling constant to be approximately  $82 \pm 1$  Hz.

There has been a large increase recently in NMR exchange studies of inorganic and organometallic systems. The halogen exchange reactions of methyltin halides (91), and of trans-dichlorobis(pyridine) platinum(II) in selected solvents (92)

have been studied. The mechanism of  $F^-$  exchange in the  $TiF_4 \cdot 2(\text{donor})$  complexes has been investigated by Dyer & Ragsdale (93). The kinetics has been obtained for triphenylphosphine exchange with the tetrahedral complexes (94) dihalobis(triphenylphosphine)-cobalt(II) and - nickel(II). In a continuation of a previous study (95), data on the ligand exchange of aminopolycarboxylic acids with the alkaline earth ions have been reported by Kula & Rabenstein (96). Zumdahl & Drago (97) have used the complete line-shape method to investigate the exchange of 2-picoline with dichlorobis(2-picoline)cobalt(II). Simpson (98) has studied the kinetics of anion exchange between methyl mercuric complexes. Brown et al. (99, 100) have continued their interesting series (See Ref. 22) of studies of organometallic exchange reactions using  $^7Li$  and  $^1H$  NMR spectra. They have investigated the stoichiometry of mixed complexes of phenyllithium with diphenyl magnesium or with diphenyl zinc in ether (99) and also discussed the various exchange processes occurring in these systems. Seitz & Brown (100) have studied the different properties

of phenyl and alkyl groups for bridge bonding and complex formation in lithium and magnesium organometallic compounds. Proton resonance studies have been made of the exchange of trimethylgallium with its several addition compounds (101). Randall, Yoder & Zuckerman (102) have investigated the exchange processes in stanylamines which involve the breakage of the Sn-N bond.

Chemical exchange has been reported for a variety of other metal-organic complexes. The N,N-dimethylformamide exchange rates in its complexes with  $\text{AlCl}_3$ ,  $\text{AlBr}_3$ ,  $\text{AlI}_3$ ,  $\text{BeCl}_2$ ,  $\text{GaCl}_3$ ,  $\text{SbCl}_5$  and  $\text{TiCl}_4$  have been determined by Fratiello et al. (103, 104). A similar study of dimethylsulphoxide exchange in complex cobalt (III) ions has been carried out by Lantzke & Watts (105); acetonitrile exchange rates in solutions of nickel (II) ions have been determined by Ravage, Lanford & Stengle (106). In a proton resonance study of cis-bis(dibenzyl sulfide)-, cis-, and trans-bis(dialkyl sulfide)dichloroplatinum(II) complexes Haake & Turley (107, 108) found that sulfur is pyramidal in these complexes and that inversion at sulfur occurs more rapidly in trans than in

cis complexes ( $E_a = 18$  kcal/mole for cis). A temperature dependence study of  $\alpha$ -cyclopentadienyl(triethylphosphine)copper(I) by Whitesides & Fleming (109) has led them to propose that the averaging of chemical shifts observed at high temperatures occurs by either 1,2 or 1,3 migration of the metal atom around the cyclopentadienyl ring. A  $^{11}\text{B}$  NMR study in aqueous solutions of boric acid and alkali meta- and polyborate salts (110) has yielded information on their polymerization equilibria. Finally, changes with temperature of the proton spectra of some isoleptic transition-metal  $\pi$ -allyl complexes have been reported (111).

#### NUCLEAR RELAXATION

The fact that nuclear relaxation processes yield important and unique information about the dynamic structure of liquids and the nature of molecular motions is shown by the numerous investigations which are now being carried out in this field. Much of the earlier work has been reviewed by Dwek and Richards (112). Our main concern here is with the more recent work dealing with nuclear relaxation in liquids and gases.

A promising new method for obtaining the relaxation behaviour of individual lines in a complex NMR spectrum has been described by Vold et al. (113). The experiment starts with a non-selective  $180^\circ$  pulse followed after a time  $\tau$  by a non-selective  $90^\circ$  pulse; then, after the latter, the entire free induction decay is recorded. The resolved spectrum is obtained from the Fourier transform of the free induction signal. The history of this spectrum as a function of  $\tau$  gives the complete relaxation behaviour of each line in the spectrum. The effects of the static field inhomogeneity are removed by applying a transient, large static field gradient between the  $180^\circ$  and  $90^\circ$  pulses.

Another paper dealing with experimental techniques is that of Hubbard & Young (114). They have performed a theoretical and experimental study of the effects of magnetic field inhomogeneities on the results of rf pulse measurements of spin-lattice relaxation times and Overhauser effects. It is concluded that for typical experimental conditions these effects are usually small

but not always negligible and that  $H_1$  field inhomogeneity has a larger effect than the  $H_0$  field inhomogeneity. The  $H_1$  field inhomogeneity can be determined from the decrease in amplitude of the signals following the  $90^\circ$ ,  $270^\circ$ , etc., pulses as the pulses become longer. The effect of magnetic field inhomogeneities on the determination of  $T_1$  by use of  $180^\circ$ -t- $90^\circ$  and  $90^\circ$ -t- $90^\circ$  pulse sequences also was calculated.

Considerable attention has been devoted to measuring relaxation times in fluorine containing compounds because the spin-rotation interaction often dominates the spin-lattice relaxation of fluorine. Slippage of electrons during molecular rotation causes a net current which generates a magnetic field. The resulting molecular magnetic moment couples with nuclear magnetic moments in the spin-rotation interaction. Fluctuations in the interaction are produced by changes in the molecular rotational state. Thus, the corresponding contribution to the nuclear spin-lattice relaxation contains information about rotational relaxation of the molecule. Extraction of that



information can present a challenge, of which an interesting example is provided by the benzotrifluorides. Dubin & Chan (115) have just measured the  $^{19}\text{F}$  spin-lattice relaxation in halo-substituted benzotrifluorides and concluded that in addition to the spin-rotation coupling due to overall rotation of the molecule there is a contribution which has its origin in coupling of the spin to internal rotation of the  $\text{CF}_3$  top relative to the frame. The latter is important in cases when no high barriers to internal rotation are present. Similar, more detailed studies have been made by Chen (116). However, the effects of the internal rotation upon the fluorine  $T_1$  were neglected in two previous studies of benzotrifluorides (117, 118).

The spin-rotation contribution to  $T_1$  depends on the elements of the tensor interaction as well as on the details of the rotational relaxation. Therefore, any quantitative check on the relaxation theory requires independent knowledge of the coupling tensor. To this end, the diagonal components of the fluorine spin-rotational tensor in the principal axis system of

fluorobenzene were determined by Chan & Dubin (119) using molecular beam magnetic resonance method. Then, by means of the relaxation theory, and using the experimental  $T_1$  data for liquid fluorobenzene reported by Powles & Green (117, 120), Chan (121) estimated the sum of the diagonal components of the fluorine spin rotation tensor. This result is in good agreement with the molecular beam measurements (119), which supports the validity of the analysis.

An opposite type of approach has been employed successfully by Bloom et al. (122, 123). The spin-rotation interaction in spherical top molecules is characterized by two coupling constants,  $C_\alpha$  and  $C_\beta$ . Molecular beam experiments yield in a straightforward way the average coupling constant  $C_a$ , but often they do not distinguish between alternative assignments for  $C_\alpha$  and  $C_\beta$  which give the same value of  $C_a$  (124). Bloom et al. (122) measured the proton and deuterium  $T_1$  in  $\text{CH}_4$  and its deuterated analogues as a function of density  $\rho$  and temperature. The proton relaxation was found to be due to the spin-rotation interaction while the

deuterium relaxation is due to quadrupole interaction. In the same study, the theory of nuclear relaxation by the spin-rotation interaction (125, 126) was extended to the case of dilute gases and spherical top molecules. On the basis of these results and additional pulse measurements of  $T_1$  for  $\text{CH}_4$  in the vicinity of the characteristic minimum (127) of the plot of  $T_1$  vs.  $\rho$ , Bloom & Dorothy (123) were able to decide between the two alternative assignments of the coupling constants  $C_\alpha$  and  $C_\beta$  for  $\text{CH}_4$  obtained from molecular beam measurements by Anderson & Ramsey (124). It seems likely that this overall approach can be applied to other molecules.

Several other studies have been made which are more or less related to spin-rotation interactions. In a continuation of relaxation studies (128-130) in systems of two-nonidentical spins MacLean et al. (131) have measured both  $T_1$  and  $T_2$  of  $^1\text{H}$  and  $^{19}\text{F}$  in  $\text{CHF}_3$  over the temperature range  $-142$  to  $-20^\circ\text{C}$ , using rf pulse methods. The results are similar to those for  $\text{CHFCl}_2$  (128, 130) in that one can distinguish different relaxation

mechanisms at low and high temperatures. In the low temperature region both  $^1\text{H}$  and  $^{19}\text{F}$  are relaxed by dipolar interactions which are predominantly intramolecular. In the high temperature region, the spin-rotation interaction is the dominant relaxation mechanism for fluorine, while the proton  $T_1$  is dipolar in origin and the proton  $T_2$  has an appreciable contribution from the scalar spin-spin interaction. Chaffin & Hubbard (132) have measured the spin-lattice relaxation, steady-state and transient Overhauser effects and diffusion coefficients of the proton and fluorine nuclei in liquid  $\text{CHF}_3$ . The Overhauser effects were found to be quite useful in separating the dipolar and spin-rotation contributions. The usual coupling between NMR and ESR is shown by the general theory of spin-rotation contributions to electron spin relaxation presented by Nyberg (133). Moreover, an extension to ESR of Hubbard's treatment (134) of nuclear spin-rotation has been developed by Atkins (135).

Interest in relaxation via quadrupole interactions seems directed mainly at implementing the proposal of Gutowsky &

Moniz (136) that such studies can be used to obtain reasonable estimates of quadrupole coupling constants in molecules. A good example of determining a quadrupole coupling constant not readily accessible by other means was given by Boden et al. (137) who estimated a value of 2.6 MHz for the  $^{11}\text{B}$  quadrupole coupling constant in dimethoxy( $\text{d}_6$ ) borane( $^{11}\text{B}$ ) from the proton  $T_1$ . Bonera & Rigamonti (138) have reported the use of quadrupole relaxation time measurements to estimate the deuterium coupling in benzene- $\text{d}_6$  and acetone- $\text{d}_6$ . From the measurements on CDFO, a deuterium quadrupole coupling constant of  $230 \pm 70$  kHz has been obtained by MacLean et al. (131). Powles et al. have investigated (139-141) liquid heavy ammonia and arrived at the conclusion that the deuterium coupling constant of  $245 \pm 25$  kHz in liquid  $\text{ND}_3$  is not very different from the value  $282 \pm 12$  kHz in the gas phase.

Nuclear relaxation times in fluids may be expressed in terms of the Fourier transforms of the relevant correlation functions of the lattice. Oppenheim & Bloom (142) have recently developed

a theory for the evaluation of the correlation functions in terms of the intermolecular forces under which the particles move.

Riehl, Kinsey & Waugh (143) have carried out calculations of  $T_1$  for  $H_2$  gas ( $J=1$ ) infinitely dilute in  $H_2$  using kinetic theory of gases with quantum cross sections. Their analysis indicates that when the Oppenheim-Bloom theory is applied to dilute gases, the results are consistent with scattering theory either for systems with short range potentials and classical dynamics (144) or long range potentials and quantum dynamics. Chen & Snider (145) in their collision theory of relaxation processes derive expressions for  $T_1$  and  $T_2$  (also for the chemical shift) in terms of the binary transition operator. Their work is based on the modified quantum mechanical Boltzmann equation. A different type of theoretical problem has been considered by Rao & Lessinger (146) who apply the density matrix method of analyzing relaxation effects in nuclear double resonance to weakly coupled spin systems of large molecules.

Spin-lattice relaxation times have been measured in a wide variety of systems (147-162). Kessler, Weiss & Witte (147) have measured the proton  $T_1$  and the self-diffusion coefficient by spin-echo methods in the liquid phase between the melting and boiling points for numerous molecules of the  $(CH_3)_4X$  type where  $X = C, Si, Ge, Sn, Pb$ . Kachaev et al. (148-150) have measured the proton spin-lattice relaxation times in a series of homologous n-paraffins and observed that the activation energy obtained from  $\log T_1$  vs.  $1/T$  plots depends upon the frequencies of deformation vibrations. The proton  $T_1$  has been determined in ethylene as a function of density and temperature by Trappeniers & Prins (151). The large decrease in the proton  $T_1$  of water due to low concentration of glycogen has been explained by Ragazzino (152) in terms of micro-viscosity effects. Eisenstadt & Friedman (153, 154) have continued their studies of  $^{23}Na$  spin-lattice relaxation in aqueous solution of various diamagnetic salts. The proton  $T_1$  of butyl phthalate has been determined at different temperatures by Lehaci (155). Boehme & Eisner (156)

have measured the chlorine  $T_2$  and the deuterium  $T_1$  and  $T_2$  in liquid HCl and DCl over the temperature range of -40 to 60°C. The chlorine measurements yield the unexpected result that the molecular reorientational correlation times increase with increasing temperature. An interpretation of this finding is given.

Nuclear relaxation studies have been carried out on several solutions containing paramagnetic species. Newmark, Stephenson & Waugh (157) have measured the proton  $T_1$  in potassium-ammonia solutions at different temperatures over a wide range of concentrations. The electron correlation time has been found to be  $4 \times 10^{-13}$  sec up to about 0.15 M potassium and decreases rapidly at higher potassium concentrations. Manley & Pollak (158) have determined proton spin-lattice relaxation times in aqueous Cr(III) solutions of varying acidity. The proton and deuterium  $T_1$  and  $T_2$  in aqueous Mo(V) solutions have been measured by Mazitov (159). The hydrated cupric ion in aqueous solutions has been investigated by Morgan et al. (160) and by Griffel (161).



The effect of hyperfine interaction on proton relaxation has been investigated by Pfeifer et al. (162) in dilute solutions of paramagnetic ions using a theoretical model of one paramagnetic ion and one proton.

Some work has been done on relaxation of solvent nuclei in several solutions of free radicals. The frequency and temperature dependence of  $T_1$  have been studied by Müller-Warmuth & Printz (163). They found that the nuclear-electron dipolar coupling, modulated by translational diffusion, is the major relaxation mechanism in most systems, whereas rotational tumbling of solvent-radical complexes is more effective in aqueous solutions. Additional data on the stable liquid free radical di-t-butyl-nitroxide were obtained from the study (164) of the concentration and temperature dependence of its ESR spectrum and of the proton relaxation times.

A phenomenon dependent upon relaxation processes is dynamic nuclear polarization (DNP) of which a perceptive review has been written by Richards (165). The experiments of interest here are

performed upon solutions of free radicals in a diamagnetic solvent. The free radical is irradiated in an ESR experiment while the nuclear resonance of the solvent is observed. As the electron spins perturbed by ESR relax, nuclei coupled to them also relax and the populations of the nuclear spin states are "pumped" away from their thermal equilibrium values. The nature and extent of this dynamic nuclear polarization are sensitive measures of the electron-nucleus interactions. An investigation of DNP at two magnetic fields for phosphorus III and phosphorus V systems has been carried out by Atkins et al. (166). The results obtained were interpreted in terms of a scalar interaction between the  $^{31}\text{P}$  nuclei and the radical electron. This interaction is more pronounced for phosphorus III compounds, the difference being explained in terms of steric hindrance about the phosphorus V compounds. A similar study of scalar interactions with  $^{31}\text{P}$  has been reported by Dwek & Richards (167). The DNP of fluorine nuclei in solutions of free radicals has been investigated by Dwek et al. (168), Poindexter, Stewart & Caplan (169), and by

Stewart, Poindexter & Potenzu (170). Stehlik & Hauser (179) have performed DNP experiments in which the relaxation of protons contained in free radicals was measured in proton-free solvents by spin-echo methods. The results were analyzed by using general relaxation theory of Abragam (172) and Solomon (173) to calculate the DNP coupling parameter for mixed scalar and dipolar intermolecular interactions modulated by electron spin relaxation and exchange and by molecular motions.

A very interesting effect has been observed in NMR studies of rapid, free radical reactions by Bargon, Fischer & Johnsen (174) and Ward & Lawler (175). Bargon et al. (174) observed changes in the NMR spectra during thermal decomposition of peroxides and azo-compounds, and found that during some reactions the reaction products show intense emission proton NMR lines. Bargon & Fischer (176) have interpreted the effect in terms of chemical'y induced dynamic nuclear polarization (CIDNP). After the formation of radical intermediates with the electron in equally populated spin states, the dynamic coupling between the relaxing,

free electrons and the protons produces the proton polarization which is transferred to the products by a secondary reaction. A theoretical analysis of this effect predicts a correct order of magnitude for the calculated intensity of emission, and the authors (176) give additional experimental results in support of the proposed interpretation. Ward & Lawley (175) have studied formation of 1-butene from n-butybromide and n-butyllithium, another reaction which proceeds through a free-radical intermediate. The NMR spectra run during the course of reaction also exhibit intense emission and absorption lines originating in 1-butene species. This effect is interpreted in terms of nuclear polarization of a free-radical intermediate which disproportionates to form olefin from which emission and enhanced absorption are observed. Lawler (177) has presented a qualitative discussion of the effect for a two spin case, i.e., one electron and one proton in a magnetic field. It seems that this phenomenon will receive considerable attention in the near future because of its relation to the details of the chemical reactions

involved.

#### CHEMICAL SHIFTS

From the large variety and number of studies dealing with theoretical and/or experimental aspects of chemical shifts we have chosen to discuss briefly the promising developments on  $^{13}\text{C}$ . We give only a few general comments on all other chemical shift investigations.

The recent improvements in NMR instrumentation, particularly the development of field-frequency stabilization techniques (178), now enable one to use time-averaging techniques for the measurement of  $^{13}\text{C}$  spectra. Grant (179) has employed an analog frequency-sweep spectrometer with proton stabilization of the magnetic field, whereas Roberts (180) uses a digital, frequency-sweep spectrometer. Maciel et al. (181) describe a procedure based on a direct  $^{13}\text{C}$  field-frequency lock system. From these results and especially those obtained by Grant et al. (182-184), it appears that  $^{13}\text{C}$  spectroscopy at natural abundance is developing into an important tool for determining molecular conformation.

As to the results themselves, Woolfenden & Grant (182) have discussed the relationship between molecular conformation and the  $^{13}\text{C}$  chemical shifts of methyl carbons in methylbenzenes. The  $^{13}\text{C}$  shifts of a number of methyl cyclohexanes measured by Dalling & Grant (183) provide additional information on steric effects. Grant & Cheney (184) have discussed a model which relates the  $^{13}\text{C}$  chemical shifts of sterically perturbed carbon atoms to sterically induced charge polarization in the  $^{13}\text{C-H}$  bond. These authors (185) have used a valence-bond approach to derive an expression for the  $^{13}\text{C}$  chemical shift and they show that changes in the paramagnetic screening term are of primary importance. Deviations from classical perfect-pairing bond structures and also the effects of steric polarization of electrons along the C-H bonds are discussed, and the theory is applied to simple alkane molecules.

Other  $^{13}\text{C}$  work includes that of Maciel et al. (181) on the deuterium isotopic shift of the carbonyl group in acetone- $\text{d}_6$  compared to that in acetone. Stothers et al. (186, 187) have

continued their  $^{13}\text{C}$  studies by measuring shifts in cyclopropyl ketones (186) and substituted methyl benzoates (187). Weiner & Malinowski (188) have studied substituted cyclopropanes, and Spielvogel & Purser (189) have correlated  $^{13}\text{C}$  and  $^{11}\text{B}$  chemical shifts for some boron-nitrogen compounds and their analogous alkanes. The anisotropy of the  $^{13}\text{C}$  nuclear shielding in methyl iodide has been found to be  $\Delta\sigma = \sigma_{\parallel} - \sigma_{\perp} = -30 \pm 3$  ppm by Yannoni & Whipple (190) in measurements carried out on liquid crystal solutions.

Interest in the spectra of partially oriented molecules continues strong. The chemical shift anisotropies obtained for  $\text{CH}_3\text{F}$  in a nematic solvent (191-193) indicate that the apparent proton shielding anisotropies depend strongly upon the technique and references used. The molecular structures of cyclopropane (194, 195), cyclobutane (194), cyclobutadiene-iron tricarbonyl (196), and s-trioxane (197) have been determined from analyses of high-resolution proton spectra obtained in nematic solvents. The results for cyclobutane (194) are of particular importance

in that they prove the carbon ring to be non-planar.

There is considerable action on the NMR contact shift front, mainly in connection with inorganic complexes. Proton contact shifts have been reviewed in detail by Dwek & Richards (20). Expressions for dipolar and Fermi-contact contributions to ligand resonance shifts in axially distorted octahedral Co(II) systems have been derived by Jesson (198), via McConnell's (199) treatment. Also, Jesson (200) combined NMR, ESR and optical data to evaluate the dipolar contribution to the proton shifts in the ligands for a variety of trigonal Co(II) and Ni(II) chelate systems. In their study of proton contact shifts in Ni(II) - benzylamine complexes, Fitzgerald & Drago (201) have concluded that the unpaired spin can be delocalized in the phenyl system when the ligand-metal interaction is essentially  $\sigma$ . Horrocks & Hutchinson (202) have measured the isotropic shifts for water protons in aqueous solutions of Co(II) containing various monodentate ligands.



Some progress has been made on the systematic measurement of  $^{14}\text{N}$  chemical shifts (203-206).  $^{14}\text{N}$  is one of the "less receptive" nuclei and in addition possesses a nuclear quadrupole moment which often leads to a broadened resonance and increased experimental difficulties. However, in compounds where the nitrogen nuclei are spin-spin coupled to protons, the  $^{14}\text{N}$  chemical shift has been obtained from the proton spectrum by double irradiation techniques (207-211). This approach should have some useful though limited applications.

A variety of other chemical shift studies have appeared. They include theoretical studies of chemical shifts (212-216), measurements of chemical shifts in aqueous solutions (217-219),  $^1\text{H}$  chemical shifts in different systems (220-229),  $^{31}\text{P}$  chemical shifts (230-232),  $^{19}\text{F}$  chemical shifts (233-245), effects of solvents on chemical shifts (246-259), and the magnetic anisotropies of different bonds (260-267).

A novel development with considerable promise of future importance has been reported by Pirkle (268). Pirkle et al.

(268-271) have found that d, l enantiomers exhibit nonequivalent NMR spectra when measured in an optically active solvent.

Similar observations were later made by Jochims et al. (272).

Chemical shifts between d and l isomers are produced by differences in their interactions with asymmetric solvent molecules.

In principle, such shifts should be a measure of optical purity and may serve as a means of determining absolute configurations of optically active molecules.

#### SPIN-SPIN COUPLING

Theoretical calculations of the indirect spin-spin coupling constant are still highly approximate. The overall problems inherent in the calculations have been discussed in considerable detail by Grant & Barfield (273) in a recent review. The starting point continues to be the general Hamiltonian formulated by Ramsey (274), which gives the coupling constant as the sum of three terms-- the orbital, the spin dipolar, and the Fermi contact contributions. Both perturbational and variational methods have been employed to evaluate the Hamiltonian. In

most of the early work, only the usually-dominant contact term was evaluated and that by means of the average excitation energy approximation, with a VB wavefunction. Recent emphasis has been on the MO theory and on means of avoiding the excitation energy approximation.

Using perturbation theory, Pople & Santry (275) have carried out an MO calculation including explicitly the lowest unoccupied orbital and thus excluding the average excitation energy approach. On the basis of their treatment they were able to show that some of the coupling constants could be negative. Their delocalized MO approach has been tried by a number of other investigators (276-278). For example, Yonezawa et al. (276) have used it to calculate H-H coupling constants for simple hydrocarbons and other compounds. The results agree qualitatively with experiment except for compounds containing heteroatoms. In a similar fashion, Murrell, Stephenson & Jones (277) have calculated the coupling constants in fluoromethanes and in the first-row fluorides.

The work by Kato & Saika (278) is a good example of the current situation. They used the Pople-Santry approach to calculate the H-F coupling constant in HF, taking into account higher unoccupied orbitals to explore the convergence of the perturbation expansion. A number of single determinant wave-functions were used for the calculation of the perturbation matrix elements. The results of the study show that the Fermi contact term is dominant for the H-F coupling, the orbital term due to first-order perturbation is negligible small, while the second-order perturbation orbital term and the spin dipolar term are 20% and 10%, respectively, of the total. They conclude that the calculated values of the coupling constants are extremely sensitive to the wave functions employed, not only for the ground state but also for the excited states. They could not establish whether the ordinary perturbation treatment of the coupling converges or not.

Another feature of the theory which is receiving significant attention is the use of the perturbation-variation method (279).

Shaefer & Yaris have employed a Hylleraas-like variational procedure (280) for calculating the coupling in HD and found that the use of a trial function with  $\delta$ -function singularities leads to ambiguous results. In fact one can obtain two different values of the coupling constant depending on the direction of integration. More rigorous procedures were proposed to remove this ambiguity. Vladimiroff & Dougherty (281) suggested an alternate way of removing the singularity terms in the trial first-order wavefunction. On the basis of their perturbation-variation calculations, Schaefer & Yaris (282) have treated in a phenomenological way the absolute signs of the spin coupling constants for the systems H-X, H-C-X, H-C-C-X, where X = D, B, C, N, O, F, and all carbons are saturated.

Several other theoretical papers in this area have attracted our attention. Hiroike (283) derived a general expression for the H-H coupling constant in saturated hydrocarbons using a double perturbation theory (280) and the average excitation energy approximation. Barfield (284) has extended the VB

theory to calculation of the coupling in  $H_2$ , in a fashion similar to the Pople-Santry treatment, by explicitly including the triplet VB wavefunction and energy in the perturbation sum.

Hecht (285) has calculated the geminal H-H coupling constant by a more rigorous treatment based on the Dirac-Van Vleck vector model.

The ability of experimentalists to determine the magnitude of coupling constants, their relative and sometimes even their absolute signs, continues to outstrip by several orders of magnitude the ability of theoreticians to use effectively these data. During the past year or so, the magnitudes and relative signs of coupling constants have been determined for a variety of systems. Included are: the H-H coupling in four and five-membered saturated ring compounds (286), in formic acid esters (287), in 2-butyne-1-ol (288), and in isopropenylacetylene; the  $^{13}C$ - $^{13}C$  coupling in acetic acid (179); the  $^{13}C$ -X coupling in  $(CH_3)_4X$ , where  $X = ^{29}Si, ^{119}Sn, ^{207}Pb$  (290), and in  $(CH_3)_2X$ , where  $X = ^{77}Se, ^{125}Te$ , (291); the  $^{13}C$ - $^{29}Si$  coupling in  $(CH_3)_4Si$

(292); the  $^{13}\text{C-H}$ ,  $^{31}\text{P-H}$ ,  $^{31}\text{P-C-H}$ , and  $\text{H-P-C-H}$  couplings in methylphosphonium ions (293); the  $^{31}\text{P-}^{19}\text{F}$  in di-isopropyl fluorophosphate (294); the  $\text{X-H}$  and  $\text{X-C-H}$  in  $(\text{C}_2\text{H}_5)_2\text{X}$ , where  $\text{X} = ^{77}\text{Se}$ ,  $^{111}\text{Cd}$ ,  $^{113}\text{Cd}$ ,  $^{125}\text{Te}$  (295); the  $^{29}\text{Si-H}$  in methylchlorosilane (296); the  $^{31}\text{P-}^{19}\text{F}$ ,  $^{31}\text{P-C-}^{19}\text{F}$ , and  $^{31}\text{P-H}$  in fluorophosphines (297); and the  $^{195}\text{Pt-H}$  coupling in square planar complexes of platinum(II) (298). The absolute sign of the  $\text{H-F}$  coupling in  $\text{CH}_3\text{F}$  has been found to be positive by Bernheim and Lavery (191) who observed the spectrum in a liquid crystal solvent.

In addition to coupling of nuclei via electrons in the bonding framework of a molecule, experimental evidence has accumulated in support of appreciable "through-space" coupling (299-300) via non-bonding electron interactions. The available evidence is strongest for the coupling of two fluorines (300-305) whose internuclear separation is  $2.0 \text{ \AA}$  to  $2.5 \text{ \AA}$ , i.e. something less than twice the fluorine van der Waals radius. Moreover, the magnitude of the coupling increases sharply with decreasing internuclear separation (303). Indirect support for such a

non-bonded coupling mechanism is provided by the dynamic nuclear polarization of  $^{19}\text{F}$  nuclei observed by Poindexter, Stewart, & Caplan (169) in solutions of free radicals. The results imply that fluorine nuclei, but not protons, in solvent molecules have appreciable hyperfine interactions with the unpaired electrons of the solute free radicals.

There have been some objections raised against the "through-space" interaction concept (300, 306) particularly for vicinal F-F coupling constants. Furthermore, it is clear that such effects are very small for H-H coupling and modest at most for H-F.

Anet, Bourn, Carter, & Winstein (307) have studied the effect of steric compression on H-H coupling constants and observed that "through-space" coupling is negligible when the interaction is directly between two nonbonded protons, but that there is a considerable contribution to the H-H coupling if the interaction proceeds via an oxygen atom (present as -O-H group). On the other hand, a long-range coupling between  $^1\text{H}$  and  $^{19}\text{F}$  separated by six bonds has been interpreted in terms of "through-space"



coupling (308).

There is a definite need for theoretical studies of non-bonded type contributions to the spin-spin coupling. Nonetheless, empirical applications of the phenomenon can be made. For example, Jonas, Borowski & Gutowsky (303) have found from an analysis of high and low temperature limits for the F-F coupling in several 2-fluoro- $\alpha$ -substituted benzotrifluorides that there is a dependence of the non-bonded coupling upon the dihedral angle between the C-F bond in the  $\text{CFX}_2$  group and that of the 2-fluorine. In turn, Jonas (309) has explained the F-F coupling in perfluoroxylens in terms of this angular dependence (303) and the conformational structure of two adjacent  $\text{CF}_3$  groups.

#### SOLID STATE

In solids, the relatively large dipole-dipole broadening of a nuclear resonance usually inhibits the observation of chemical shifts and/or the indirect spin-spin coupling. As a consequence there has been considerable interest in methods

designed to eliminate the dipolar broadening or to separate its effects in some manner from those of other interactions. The first step in this direction was the independent discovery by Andrew et al. (310) and by Lowe (311) that high-speed rotation of a solid sample about an axis at the "magic angle" of  $54.70^\circ$  with respect to the direction of the magnetic field removes the dipolar broadening and permits observation of chemical shifts (312)

recent report by Kessemeier & Norberg (313) of pulsed NMR measurements on rapidly rotating solid samples includes most of the relevant references on this technique and also gives a stochastic theory for the transverse and longitudinal spin relaxation processes. As in the NMR spectra of liquids, the observation of samples rotated at the magic angle yields only the isotropic chemical shift,  $\sigma = (1/3) \text{Tr } \underline{\underline{g}}$  where  $\underline{\underline{g}}$  is the nuclear shielding tensor. Thus, information about the anisotropy of  $\underline{\underline{g}}$  is lost. Multiplets due to the indirect spin-spin coupling have been resolved by Andrew et al. (314) in solid samples of

$\text{KAsF}_6$  and  $\text{KSbF}_6$  using the rotating sample technique. Thereby, it was finally established that the fine structure observed in the  $^{123}\text{Sb}$  resonance of aqueous solutions of  $\text{KSbF}_6$  results from indirect rather than from direct dipole-dipole coupling.

The averaging out of dipolar broadening by dynamic processes has now been extended to include the use of strong rf fields. Recent experiments (315, 316) have demonstrated that dipolar interactions in solids can be removed or reduced with a modified Carr-Purcell spin-echo technique (317). However, these experiments also remove the effects of chemical shifts and indirect spin-spin coupling. A theory for multiple spin echoes in such cases has been given by Waugh & Wang (318). A more recent rf pulse method, developed by Waugh & Huber (319), has the important advantage that it permits observation of the chemical shift anisotropy in solids.

The new method is based on applying a train of phase-alternated  $90^\circ$  pulses which attenuates the dipole-dipole broadening but preserves chemical shifts and indirect spin-spin

couplings. A theoretical analysis of this experiment and of the general behaviour of a spin system disturbed by a train of closely spaced pulses has been developed by Waugh et al. (320). The authors propose two new experiments involving complex pulse sequences. The first is performed on liquids, and yields an arbitrary, adjustable scaling of chemical shifts in the high-resolution spectrum. This experiment could prove useful in the analysis of complex spectra, though it does require taking a Fourier transform of the induction signals. The other experiment, on solids, removes completely dipole-dipole and quadrupole interactions and thus permits the measurement of chemical shift anisotropies and spin-spin couplings.

The broadening of rigid-lattice line shapes by the combined effects of two or more types of interaction has attracted some attention. One case relates to determination of the M-H bond distances in  $\text{HCo(CO)}_4$  and  $\text{HMn(CO)}_5$  from the proton resonance. Analysis of the line shape and second moment  $M_2$  on the basis of dipolar interactions alone leads to exceptionally short distances

of 1.42 Å and 1.28 Å. However, the quadrupolar metal nucleus may be coupled to an electric field gradient along the molecular symmetry axis. The dipole-dipole interactions of a spin-1/2 nucleus with such a quadrupole coupled nucleus have been calculated by VanderHart, Gutowsky, & Farrar (321) for a two-spin (1/2, 7/2) system as a function of the ratio of quadrupole coupling to Zeeman energy of the spin-7/2 nucleus. In the limit of large quadrupole coupling, the  $M_2$  of the spin-1/2 nucleus is 1.84 times its value for zero quadrupole coupling, and the true M-H bond distance is correspondingly less.

The effects of anisotropic chemical shifts upon high-field, rigid-lattice NMR lines have been investigated (322) for cases in which both direct and indirect dipolar interactions are present. General second and third moment expressions are given, good to first order, including all three perturbations. It is shown rigorously that the contribution of the anisotropic chemical shift to  $M_2$  is always completely separable from the dipolar contributions. The more complex results for the third moment may

be useful in determining the sign of the chemical shift anisotropy. Also, theoretical line shapes are calculated for some two-spin systems for polycrystalline samples, assuming axial symmetry at the nucleus being observed and including the anisotropic chemical shift, direct, and indirect dipolar interactions. The results suggest that complete line shape analyses will be possible in few cases.

A considerable variety and number of experimental studies have been made. Among these are several dealing with quadrupole coupling constants. Chiba (323) has found the deuterium quadrupole coupling constant to be 327.0 kHz at 77° K in LiOD using single crystal, wide-line measurements. A deuterium quadrupole coupling constant of  $180.1 \pm 1.0$  kHz has been determined by Linzer & Forman (324) in a single crystal of ND<sub>4</sub>Cl. Also, the electric field gradient tensor has been evaluated by Bjorkstam (325) for the deuterium sites above and below the Curie temperature in crystals of deuterated tri-glycine sulfate and KD<sub>2</sub>PO<sub>4</sub>.

O'Reilly et al. have carried out a very detailed NMR study of ferroelectric ammonium sulfate (326) and ammonium fluoroberyllate (327) and their deuterated analogues in order to improve our understanding of the many similarities and differences in their crystal structure and properties. In this work, the deuterium resonance, and the  $^1\text{H}$  and  $^{19}\text{F}$  spin-lattice relaxation time  $T_1$  and their relaxation time along the rf field  $T_{1\rho}$ , were measured from  $77^\circ\text{K}$  to  $500^\circ\text{K}$ . The results of the measurements of the deuterium  $T_1$  relaxation times in  $(\text{ND}_4)_2\text{SO}_4$  by Kydon, Pintar & Petch (328) are in agreement with the interpretations given by O'Reilly et al. (326).

Haupt & Müller-Warmuth (329) have studied dynamic nuclear polarization, and the proton and electron relaxation in several organic polycrystalline free radicals and discussed their experimental results in terms of a scalar nuclear-electron interaction in which the electron-electron exchange coupling has a random time dependence. In a similar vein, Haupt & Müller-Warmuth (330) have investigated both theoretically and experimentally the

proton relaxation in organic solids due to the interactions with paramagnetic free radicals.

Line shape and relaxation time measurements continue as an important means of investigating the dynamic structure of solids. The ion motion in tetrafluoroborate salts has been studied by Caron et al. (331) who carried out wide-line and spin-lattice relaxation time measurements. Similar studies of molecular motions have made in urea-d<sub>4</sub>-n-hydrocarbon and urea-d<sub>4</sub>-fatty acid adducts (332), in several silicon-nitrogen compounds (333), and in a series of solid ethers (334). A temperature dependence study of <sup>1</sup>H and <sup>19</sup>F second moments and T<sub>1</sub> in solid ammonium heptafluorozirconate has been reported by Pintar, Lahajnar & Slivnik (335). The sudden change in second moment around 62°C from 5 Gauss<sup>2</sup> at lower temperatures to 0.5 Gauss<sup>2</sup> in solid 1,1,1,2-tetrachloro-2-methylpropane has been interpreted by Kolde & Oda (336) in terms of fast rotation of the molecule in the crystal lattice in the high-temperature phase.



McCall (25) has presented a survey of relaxation studies in solid polymers and has compared the frequency and temperature dependence of dielectric, mechanical, and NMR relaxation for a number of polymers. He finds a good correlation among these methods and emphasizes the importance of comparative studies. Woessner & Snowden have detected the lambda transition in  $\text{NH}_4\text{Br}$  and  $\text{ND}_4\text{Br}$  (337, 338) and in  $\text{NH}_4\text{Cl}$  and  $\text{ND}_4\text{Cl}$  (339) from proton and deuterium  $T_1$  temperature dependence measurements. They show that earlier attempts were unsuccessful because of large thermal gradients in the samples. Their results add substantially to our understanding of the dynamics of the order-disorder transition in these perennial favorites.

Tarr, Stacey & Briscoe (340) have measured  $T_1$  for the  $^{79}\text{Br}$  and  $^{81}\text{Br}$  species in  $\text{NaBr}$  and  $\text{LiBr}$  and for the  $^{127}\text{I}$  species in  $\text{NaI}$  and  $\text{RbI}$  in the temperature range 15-77.3° K, and at room temperature. Haberlein & Maier (341) report the temperature dependence of the spin-lattice relaxation in polycrystalline benzene and show that their calculated values of  $T_1$  are in good

agreement with the experimental data. Finally, Blinc & Lahajnar (342) made an interesting discovery in their study of spin-lattice relaxation times of  $\text{SF}_6$ ,  $\text{SeF}_6$  and  $\text{TeF}_6$  by pulse methods both in the liquid and solid state. The authors present the first experimental evidence that there is spin-rotation interaction in some molecular solids with a high degree of reorientational freedom and that within certain temperature regions it can be the dominant  $T_1$  relaxation mechanism.

#### BIOLOGICAL APPLICATIONS

Very recently there has been a rapid increase in the number of NMR studies of biological systems. This trend seems to be due mainly to improvements in instrumentation. The great potential of NMR for studying various biological problems has been recognized for some time. However, inadequate sensitivity and overlap of the many resonances belonging to various non-equivalent but closely similar protons hampered early NMR studies of biological systems. Both the sensitivity and the separation of chemically shifted lines increase with the strength of the

applied magnetic field so it was obvious that the higher the magnetic field the better the chance of obtaining useful structural information.

In this connection, the introduction of high-frequency, high-resolution proton spectrometers using superconductivity magnets (343) can be regarded as a major advance. This view is supported by the work of McDonald, Phillips & Lozar (344) who measured high-resolution spectra of DNA at 220 MHz. They found that the two methyl-thymine proton resonances due to the presence of either purine or pyrimidine in the 5' neighbor position to thymine can be used to determine the frequency of occurrence of purine vs. pyrimidines in DNA obtained from different species. Such detailed analysis was not possible in their earlier study of DNA (345) with a 60 MHz spectrometer. The advantages of working at higher frequencies are shown clearly by McDonald & Phillips (346) in their study of the conformational changes during denaturation of ribonuclease, lysozyme and cytochrome c. Again, such detailed results on the tertiary

structure of a protein could not be obtained in the pioneering NMR study of ribonuclease by Saunders et al. (347), who used a 40 MHz spectrometer. In another high-frequency study, Sternlicht & Wilson (348) followed the changes in the aromatic methyl region of the NMR spectrum of lysozyme due to denaturation; their results indicate that unwinding of the helical region occurs simultaneously with the opening up of the protein.

The chief disadvantage of the superconducting, high-frequency spectrometer appears to be its high cost, both initially and in operation. Therefore, it is not surprising that a variety of NMR studies of biochemical and biological systems were reported in 1967 using 100 MHz and/or 60 MHz high-resolution proton spectrometers. The helix-coil transitions in model polypeptides were studied by Stewart, Mandelkern & Glick (349, 350) by Markley, Meadows & Jardetzky (351), and by Ferretti (352). The substrate binding by alcohol dehydrogenases has been investigated by Hollis (353); the changes in the proton spectrum of acridine due to presence of DNA have been interpreted by Blears & Danyluk (354)

in terms of binding of acridine to DNA. The interaction between adenine, guanine and thymine in deoxyoligonucleotides has been followed in D<sub>2</sub>O solutions by Scheit, Cramer & Franke (355). The structures of serine (356), DL-threonine, and DL-valine (357) have been investigated. In the study of several amino acid-glycyl dipeptides (358) it was found that the protons of the glycyl methylene group are nonequivalent. Spotswood, Evans, & Richards (359) have studied enzyme-substrate interactions by following changes in <sup>1</sup>H or <sup>19</sup>F chemical shifts of a substrate which exchanges rapidly between solution and the actual site of the enzyme. Burgen et al. (360) have investigated the hapten-antibody complex by measuring the changes in spin-spin relaxation due to complex formation.

In their NMR review Dwek & Richards (20) have discussed in considerable detail two NMR techniques especially suited for the study of proteins: the halogen ion probe technique (361) and the proton relaxation enhancement (PRE) technique (362). The <sup>35</sup>Cl resonance has been used to study antibody-hapten

interactions (363), sulfhydryl groups of hemoglobin (364), and the helix-coil transition in synthetic poly-L-glutamate (365). The PRE technique was employed by Cohn et al. (366, 367) to investigate the enzyme-metal-phosphoryl bridge complex in the fluorokinase reaction (366), and the interactions of tetrahydrofolate synthetase with its substrates (367).

Other NMR studies include the work of Sheard et al. (368) on the binding of manganese ions to Escherichia coli ribosomes, and several  $^{23}\text{Na}$  resonance investigations of complexing of  $\text{Na}^+$  with biomacromolecules (369, 370). The deuteron resonance provides evidence that the methyl group of methionine is the source of the ring-methyl group in vitamin  $\text{K}_2$  and the C-methyl and O-methyl groups of the ring of ubiquinone in Escherichia coli (371). The existence of immobilized water in lipids (372) both in vitro and in vivo has been proved by  $T_2$  measurements.

## ION CYCLOTRON RESONANCE

Ion cyclotron resonance (ICR) shows much promise as a means of studying complex reactions between ions and molecules in the gas phase. We decided to comment on the recent studies dealing with ICR spectroscopy because of the similarities between ICR and NMR. Moreover, the ion-cyclotron double-resonance technique just introduced by Baldeschwieler et al. (373) is a major improvement of the original ICR spectrometer described by Wobschall, Graham & Malone (374), which adds greatly to the potential of the field.

ICR line-shapes can be described by phenomenological equations similar in form to the Bloch equations in NMR. Furthermore, the formalism used to calculate ICR line-shapes in the presence of charge transfer and chemical reactions is completely analogous to the coupling by chemical exchange processes of the equations of motion for the nuclear magnetization. In the one case reported thus far in detail, Beauchamp (375) gives the theory of collision broadened ICR spectra for charge transfer between ions

A and B; that is, for the reaction  $A^+ + B \rightleftharpoons B^+ + A$ .

Detailed information about the nature of the reacting species in complex ion-molecule reactions can be obtained by using the ion-cyclotron double resonance technique (376). In a mixture of ions and neutral species the equations of motion for the various components are coupled by processes such as charge transfer and chemical reaction. The existence of such coupling can be demonstrated by heating one type of ion with a strong rf electric field  $E_2(t)$  at its resonance frequency  $\omega_2$ . This produces a change in the ICR line-shape of the other ionic species in equilibrium with the irradiated ion, because the ion-molecule collision cross sections are strongly dependent on the relative ion-molecule velocity.

The resultant changes in line shape can be observed with a weak rf electric field  $E_1(t)$  at frequency  $\omega_1$ . In this manner, multiple resonance experiments can be used to identify reactant ions in a mixture even in the presence of competing processes. Reports of such studies have been given for the reaction



$\text{CD}_4^+ + \text{N}_2 \rightarrow \text{N}_2\text{D}^+ + \text{CD}_3$  (373,, for the ion-molecule reactions  
in chloroethylene (376), and for charge transfer among isotopes  
of rare gases (377).

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13. Abstract:

An annual review is given of NMR publications which appeared in 1968. Due to the exponential growth of publications dealing with NMR, it has become a necessary, common practice to cover only selected topics in the annual review and to include only selected references. Such selection usually reflects the personal interests of the reviewer, and this chapter is no exception. NMR publications are now appearing at a rate of 550 per month, which is more than an order of magnitude larger than we can cover. Most of the work omitted consists of system-oriented studies in which NMR is applied to a particular chemical system or problem, i.e. NMR is used as a tool.

We have sought to include publications emphasizing phenomena, new experimental and theoretical methods, and new areas of application. About half of our review is devoted to two ~~very~~ active fields, exchange processes and nuclear relaxation. These are followed by shorter commentaries on chemical shifts, the indirect spin-spin coupling, solid-state studies, and biological applications. We conclude with brief mention of the promising new field of ion cyclotron resonance.



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